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Coordination States of Some Metal Ions on Silica Gel Surface

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In connection with solid acidities and catalytic activities, coordination states of Mn, Co, Ni, Cu and Zn ions in the metal ion-exchanged silica gels have been investigated by means of electronic spectra, magnetic susceptibilities and ESR spectra.

It was revealed that metal ions exchanged with acidic hydrogens of surface silanol groups to form siloxane ions. Each metal ion was stabilized in divalent and high spin states in the range of dilute concentration (<1.2 wt%).

Experimental results suggested that in the evacuated samples, Mn(II) and Ni(II) ions were in octahedral ligand field, Cu(II) in tetragonal, Co(II) in both octahedral and tetrahedral and Zn(II) in tetrahedral one.

INTRODUCTION

Silica gel itself is not so much acidic, but it is found that acid sites are created on the surface when it is halogenated by the treatment with aqueous solutions of ammonium halides followed by heat treatments.¹⁾ In the previous work, the authors investigated the acidities and the catalytic activities of the halogenated silica gels and proposed the mechanism of enhancement of the acidities in silica gels by halogenation.²⁾ As a further work on the surface acidity of silica gel, the influence of some transition metal ions was investigated and it was found that metal ions exchange protons of surface silanol groups on silica gels and acid sites are created as well as in the case of halogenation.³⁾ The observation is interesting in connection with the mechanism of enhancement of acidities in zeolites exchanged with multivalent cations.⁴⁾

It is very probable that the kind of metal ions and their coordinated states affect the acidic nature of metal ion-exchanged silica gels. Investigations on this line are very few and only an example is that Hathaway's work which discussed the coordinated states of metal ions (Ni, Co and Cu) on silica gels with the aid of electronic spectroscopy.⁵⁾

Present work is mainly concerned with the coordinated states of divalent manganese, cobalt, nickel, copper and zinc ions exchanged on silica gel surface.

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EXPERIMENTAL

1. Materials

Silica gels used in the present study were prepared by hydrolysis of purified ethyl orthosilicate. The BET surface area of the gel measured by N_2 adsorption at 77°K was 660 m²/g. Transition metal ion-exchanged silica gels were prepared as follows. The silica gel was put into an ammonium acetate solution which dissolved metal chloride or nitrate and was adjusted to pH 8.0 by a NaOH solution. The solution was stirred at room temperature for a given time. Gradual decrease in pH was observed during the procedure and from extent of the decrease in pH, the amount of isolated protons was determined. The samples were washed and dried after a given time and the content of metal ions was analyzed by EDTA titration method. The amount of chlor ions on the samples was analyzed by potentiometric titration.

2. Procedure

Magnetic susceptibilities of the samples evacuated (10^{-2} Torr) at a given temperature and sealed in glass capsules were measured by a Shimadzu MB-2B type magnetic balance in the range of 77°K~273°K (temperature was raised at a rate of 1°K/min) or 20°C~500°K (at a rate of 10°C/min).

About 1 g of samples were put into a quartz cell of 1 mm thickness and electronic spectra of them were taken on a Shimadzu MPS-50L spectrometer at room temperature by diffuse reflectance method after evacuation at a given temperature.

ESR spectra of the samples evacuated at 300°C or 350°C were recorded by a JEOL-3BSX type spectrometer (X-band) at 77°C. For the measurement of g value, Mn(II) doped in MgO was used as a standard material.

RESULTS

1. On the anions in the evacuated samples

Anions of starting metal salts have a profound influence upon the rate of metal ion-exchange reaction,³⁾ therefore it is expected the anions are adsorbed

Table 1. The Amounts of Isolated Protons and Adsorbed Chlor Ions in Metal Ion-exchanged Silica Gels.

salts	amount of exchanged metal ions (m mol/g)	amount of isolated protons	amount of adsorbed chlor
		amount of exchanged metal ions	amount of exchanged metal ions
MnCl ₂	0.0175	1.20	
CoCl ₂	0.039	1.08	2.1
Co(NO ₃) ₂	0.36	0.89	
NiCl ₂	0.0426	1.93	1.9
Ni(NO ₃) ₂	0.30	1.82	
CuCl ₂	0.194	0.78	1.8
ZnCl ₂	0.226	2.32	1.8

on the metal ion-exchanged silica gels. Table 1 shows the amounts of isolated protons by the exchange reaction and the amounts of adsorbed chlor ions in the samples prepared from metal chloride solutions ($\text{MeCl}_2\text{-SiO}_2$) and evacuated at 100°C .

The amounts of isolated protons are almost independent of anions, but depend on metal ions and for Mn, Co, Cu ions, about one proton was isolated by one metal ion, while for Ni and Zn ions about two protons were isolated by one metal ion.

The amount of adsorbed chlor ions was about two times of the amount of exchanged metal ions and the ratio is independent of metal ions. To determine the conditions for the removal of anions, the thermal stabilities of them were investigated. When $\text{MeCl}_2\text{-SiO}_2$ samples were evacuated at higher temperatures (200° , 300° , 400°C), it was ascertained qualitatively that the content of chlor ions in the samples decreased with rising of evacuated temperature but it was not able to analyze the content quantitatively owing to difficulty of dissolution of metal ions into a dilute nitric acid solution. So another method, spectroscopic method, was used to ascertain the removal of chlor ions.

A series of samples were prepared from the cobalt fluoride, chloride, bromide and iodide solution respectively and electronic spectrum of each sample evacuated at 300°C was measured. A $d-d$ transition band of cobalt ions in the neighborhood of $650\text{ m}\mu$ showed "blue-shift" in order of spectrochemical series. This observation shows small amount of halogen anions remained on the surface of even the sample evacuated at 300°C .

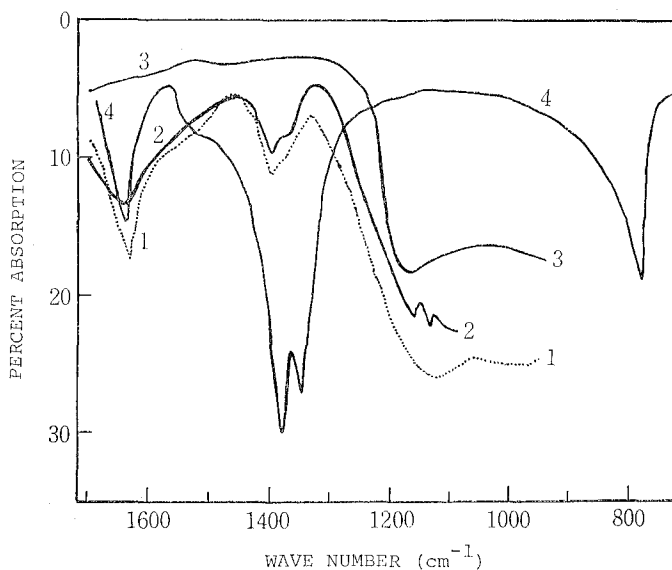


Fig. 1. IR Spectra of $\text{Co}(\text{NO}_3)_2\text{-SiO}_2$.

Co(II) content: 0.3 mmol/g

Samples were evacuated at 100°C (curve 1), 150°C (curve 2) and 300°C (curve 3) for 1 hr.

Curve 4 shows the spectrum of hexa-aquo-cobalt nitrate crystals measured by reflection method.

The behavior of nitrate ions in the samples prepared from metal nitrate solution ($\text{Me}(\text{NO}_3)_2\text{-SiO}_2$) were investigated by infrared spectroscopy. In Fig. 1 the spectra of $\text{Co}(\text{NO}_3)_2\text{-SiO}_2$ are shown as an example. The absorption band in the neighborhood of 1370 cm^{-1} is due to N-O bending mode in nitrate ions and was very strong in hexa-aquo-cobalt nitrate. When the sample is evacuated at 100° and 150°C , the band intensity decreased and no absorption was observed for the sample evacuated at 300°C .

From the results mentioned above, it can be concluded that nitrate anions can be removed by evacuation at 300°C , but it is difficult to remove chlor ions from the surface of silica gels by evacuation at 300°C . Therefore in the subsequent experiments, $\text{Me}(\text{NO}_3)_2\text{-SiO}_2$ samples were mainly used.

2. Magnetic Susceptibilities

Figure 2 shows the change of magnetic susceptibilities per 1 g sample, $\chi_{g(\text{sample})}$, for the samples exchanged with Co and Ni ions and evacuated at 100°C . The linear relationship between $\chi_{g(\text{sample})}$ and the content of metal ions were observed to indicate metal ions to be paramagnetic without spin-spin interaction in the investigated samples.

In Fig. 3 temperature dependence of magnetic susceptibilities per 1 g Ni ion, $\chi_{g(\text{Ni})}$, in the $\text{Ni}(\text{NO}_3)_2\text{-SiO}_2$ samples is shown. For comparison, $\chi_{g(\text{Ni})}$ of hexa-aquo-nickel nitrate crystal is included. $\chi_{g(\text{Ni})}$ of nickel nitrate crystal changed drastically at 170°C and simultaneously the crystal changed to a black mass with evolution of yellow brown gas. On the other hand, in the case of $\text{Ni}(\text{NO}_3)_2\text{-SiO}_2$ sample containing rather small amount of Ni ions (0.31 mmol/g), a linear

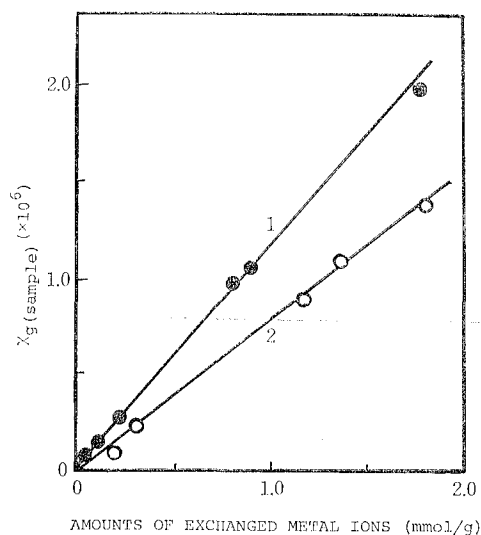


Fig. 2. Magnetic susceptibilities per 1 g samples of cobalt and nickel ion-exchanged silica gels measured at room temperature.
1: cobalt 2: nickel

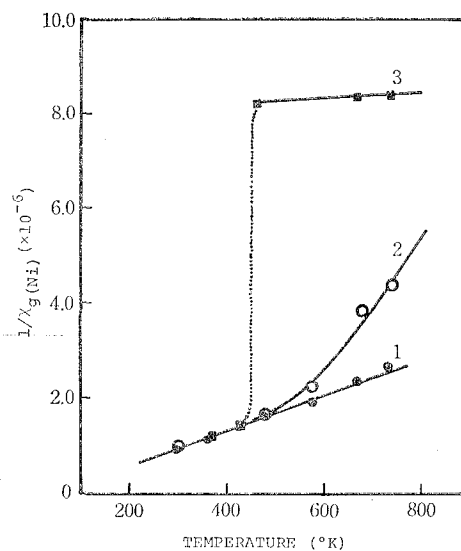


Fig. 3. Magnetic susceptibilities per 1 g nickel of $\text{Ni}(\text{NO}_3)_2\text{-SiO}_2$.
1: $\text{Ni}(\text{NO}_3)_2\text{-SiO}_2$ (Ni 0.31 mmol/g).
2: $\text{Ni}(\text{NO}_3)_2\text{-SiO}_2$ (Ni 1.20 mmol/g).
3: $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ crystal.

relationship between $1/\chi_g(\text{Ni})$ and T was maintained to higher temperatures and this relation was reversibly held when measuring temperatures were changed from high temperatures to low temperatures. The observation shows Ni ions are stabilized in divalent state on the samples evacuated above 400°C . For the sample containing rather large amount of Ni ions (1.20 mmol/g), the linear relationship deviated above 400°C and simultaneously color of the sample changed to black. The deviation seems to show the formation of nickel metal clusters by heat treatment as reported by Yates⁹⁾ about the nickel ion on carriers. In order to detect nickel metal clusters on the surface, X-ray diffraction of the sample was measured but any diffraction lines due to nickel metal were not observed. Therefore, nickel metal is probably dispersed in the form of very fine crystallites.

Magnetic moments of metal ions on the silica gel surface were determined by measurements of χ_g in the range of $77^\circ\text{K} \sim 273^\circ\text{K}$ for the samples evacuated at 300°C . In Figs. 4 and 5 some examples are shown and effective Bohr magneton numbers (μ_{eff}) are listed in Table 2.

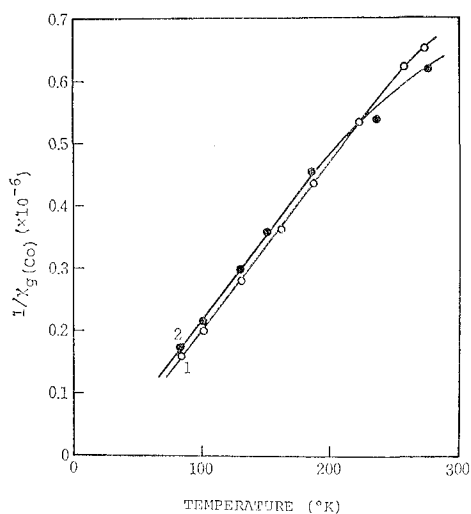


Fig. 4. Magnetic susceptibilities per 1 g cobalt.

- 1: $\text{Co}(\text{NO}_3)_2 \cdot \text{SiO}_2$ (Co 0.15 mmol/g) evacuated at 300°C , 3 hr.
2: $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ crystal evacuated at 100°C , 3 hr.

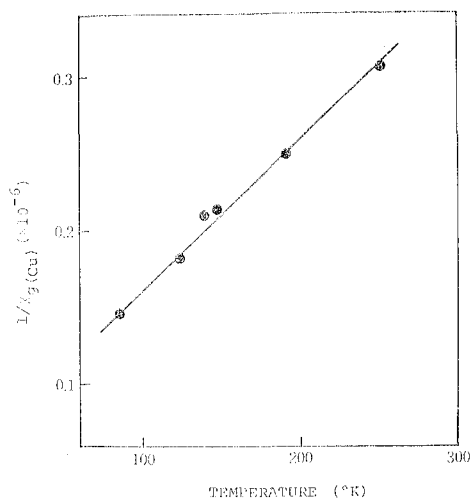


Fig. 5. Magnetic susceptibilities per 1 g copper. $\text{CuCl}_2 \cdot \text{SiO}_2$ (Cu 0.30 mmol/g)

Table 2. Magnetic Moments of Metal Ions on Silica Gel.

Metal ion	Mn	Co	Ni	Cu	Zn
Content (mmol/g)	0.23	0.30	0.15	0.30	0.27
μ_{eff} (B. M.)	6.0 ₄	4.8 ₇	3.2 ₂	1.9 ₃	0
expected number of unpaired electrons	5	3	2	1	0

3. Electronic spectra

Electronic spectra of the metal ion-exchanged silica gels were measured by diffuse reflectance method. As shown in Fig. 6 nickel ions on the silica gels exhibited their adsorption maxima at 690, 410 $m\mu$ and near 280 $m\mu$. The spectra resembled that of hexa-aquo-nickel nitrate. In the case of cobalt ions, the ab-

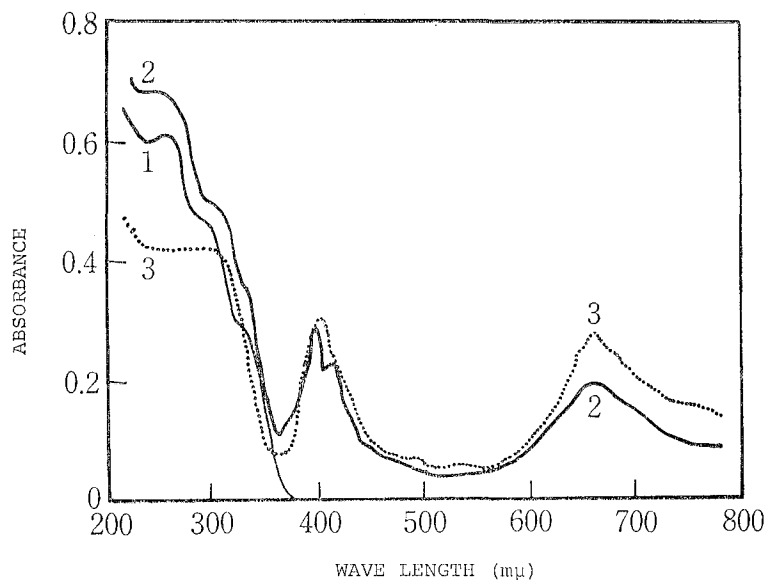


Fig. 6. Electronic spectra of $\text{Ni}(\text{NO}_3)_2\text{-SiO}_2$.

1: SiO_2 , evacuated at 400°C , 3 hr.

2: $\text{Ni}(\text{NO}_3)_2\text{-SiO}_2$ (Ni 0.33 mmol/g) evacuated at 350°C , 3 hr.

3: $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ crystal evacuated at 100°C , 1 hr.

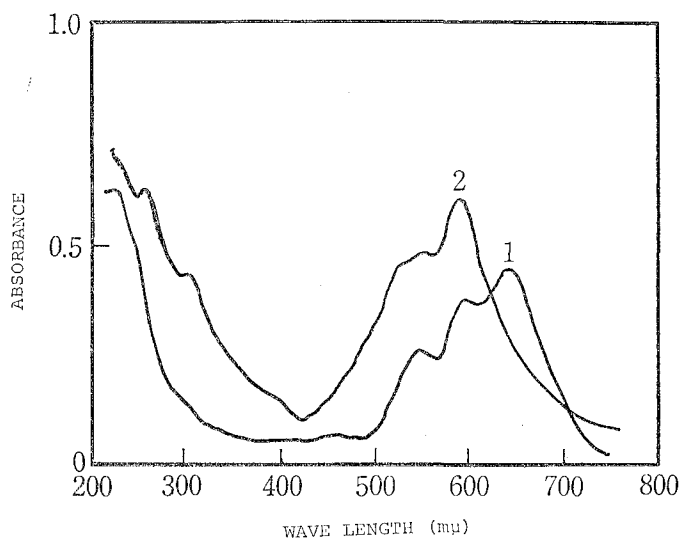


Fig. 7. Electronic spectra of $\text{Co}(\text{NO}_3)_2\text{-SiO}_2$.

1: $\text{Co}(\text{NO}_3)_2\text{-SiO}_2$ (Co 0.31 mmol/g) evacuated at 350°C , 3 hr.

2: $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ crystal evacuated at 100°C , 1 hr.

sorption maxima were observed at 660, 590 m μ for the sample evacuated at 350°C as shown in Fig. 7. The spectra of the sample evacuated at 100°C resembled that of hexa-aquo-cobalt nitrate.

Copper, manganese and zinc ions-exchanged samples did not exhibit clear absorption maxima, when they were evacuated at 350°C.

4. ESR spectra

The samples containing manganese ions more than 0.12 mmol/g exhibited ESR spectra of symmetrical singlet ($g=2.00$), while when the content of manganese ions was reduced to 0.044 mmol/g, a spectrum with h.f.s. was observed similar to Fig. 8. The resolution of h.f.s. became clearer by adsorption of ammonia at a pressure of 5 Torr as shown in Fig. 8 and g value and h.f.s. coupling constants in both spectra were the same as those of manganese (II) ions doped in MgO.

Cobalt ions on the silica gels only exhibited a broad signal even in the case of small contents of cobalt ions because of a short spin-lattice interaction time.⁷⁾

An asymmetrical spectrum with h.f.s. was observed for the samples containing copper ions as shown in Fig. 9. Principal g values were 2.066 and 2.280 corresponding to g_{\perp} and g_{\parallel} , respectively.

Nickel and zinc ions on silica gels did not exhibit ESR signals.

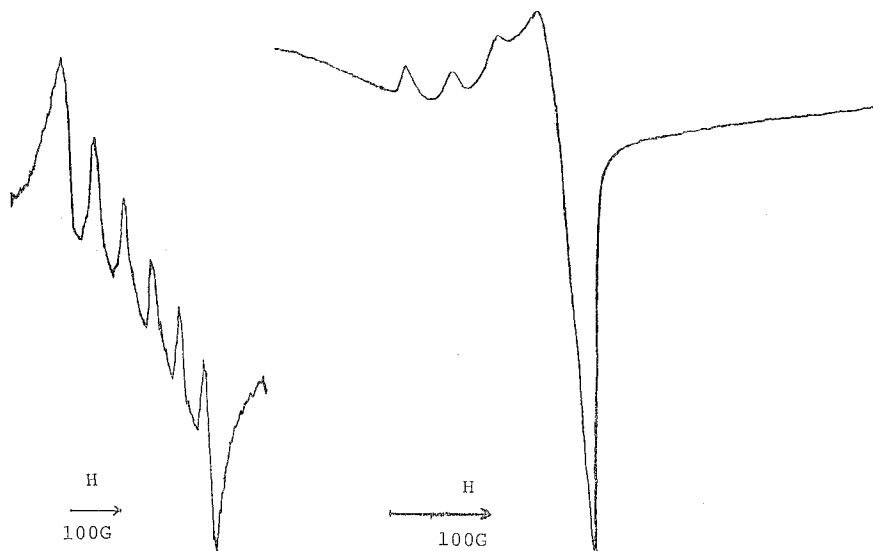


Fig. 8. ESR spectrum of $\text{Mn}(\text{NO}_3)_2\text{-SiO}_2$ adsorbing NH_3 at 5 Torr after evacuation at 300°C, 3 hr.
Mn(II) content : 0.044 mmol/g.

Fig. 9. ESR spectrum of $\text{Cu}(\text{NO}_3)_2\text{-SiO}_2$ evacuated at 350°C, 3 hr.
Cu(II) content : 0.30 mmol/g.

DISCUSSIONS

1. On the site occupied by metal ions

The liberation of protons was observed when silica gels were treated by

metal salts solution. The observation shows metal ions exchanged with acidic hydrogens of surface silanol groups to form siloxane ions. The ratio of amounts of isolated protons to the amounts of metal ions (Table 1) suggests manganese, cobalt and copper ion are coordinated by one siloxane ion, while nickel and zinc ion are by two siloxane ions.

Each metal ion investigated here has ionic radius as follows Mn: 0.80 Å, Co; 0.72 Å, Cu; 0.72 Å, Ni; 0.69 Å, Zn; 0.71 Å.⁸⁾ Therefore a tendency can be observed that larger ions are coordinated by one siloxane ions, while smaller ions are by two siloxane ions.

But, as difference of ionic radii between Co, Cu and Ni, Zn is very small, it can be hardly concluded that ionic radius is the main factor to determine the number of siloxane ions coordinated and another reasons should be sought, for example, effect of crystal stabilization energy for metal ion as discussed by Hathaway.⁵⁾

2. Coordinated states of metal ions

From the experimental results mentioned above, the coordinated state of each metal ion on the surface of silica gel can be discussed.

Manganese ion; As shown in Table 2, magnetic moment of manganese ion was 6.0 B. M. which corresponds to the expected value of 5.91 assuming number of unpaired electrons to be 5 (divalent manganese ion). ESR spectra of the sample resembled that of Mn(II) ion doped in MgO, especially when ammonia gas was adsorbed. As Mn(II) ion in MgO is coordinated octahedrally by oxygen ion, the observation suggests that manganese ions on the surface of silica gel are coordinated octahedrally by H₂O, OH⁻ and one siloxane ion.

Cobalt ion; Magnetic moments of divalent cobalt ion-complexes have been extensively investigated and it is known μ_{eff} are in the range of 4.2~4.7 B. M. and 4.7~5.4 B. M. in high spin type tetrahedral and octahedral complexes, respectively.⁹⁾ The observed value of 4.87 B. M. shows cobalt ions are in high spin type complex and coordinated octahedrally rather than tetrahedrally on the surface. The authors found magnetic moment of cobalt ions in hydrated zeolite is 5.2 B. M. Therefore there is a possibility of existence of both tetrahedrally and octahedrally coordinated cobalt ions on the silica surface.

In fact, electronic spectra ascertained the existence of tetrahedrally coordinated cobalt ions. Hexa-aquo-cobalt nitrate exhibited an absorption maximum at 595 m μ due to a *d-d* transition of ${}^4T_{1g} \rightarrow {}^4A_{2g}$ in octahedral complex.¹⁰⁾ On the other hand for the sample evacuated at 350°C three bands of 660, 590 and 550 m μ were observed. These absorption bands can be assigned to *d-d* transitions of ${}^4A_2 \rightarrow {}^4T_1$ in distorted tetrahedral field.¹⁰⁾ Absorption coefficient (ϵ) in octahedral coordination is less than that in tetrahedral coordination in one order and a weak absorption due to ${}^4T_{1g} \rightarrow {}^4A_{2g}$ is hardly detectable even if present. Judging from both magnetic moment and electronic spectra cobalt ions may be existed in both octahedral and tetrahedral coordination.

Nickel ion; Magnetic moments of nickel ions can be also as a criterion of the structure and it is known square planar complexes are diamagnetic while

octahedral and tetrahedral complexes are paramagnetic species, the magnetic moments of which are 2.9~3.3 B.M. (octahedral) and 3.6~4.0 B.M. (tetrahedral).⁹⁾ The observed value in the present investigation was 3.2 B.M. showing nickel ions to be stabilized in octahedral field in the samples evacuated at 300°C.

The stereochemistry of nickel ions complex mentioned above is ascertained by electronic spectra. The spectra of the sample evacuated at 350°C exhibited absorption maxima at 690 and 140 m μ which can be assigned to $d-d$ transition bands in octahedral complexes (690 m μ ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F), 410 m μ ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P)¹¹⁾). Recently, Hathaway investigated magnetic moments and electronic spectra of nickel ions on silica gels which are evacuated at rather lower temperatures (less than 100°C) and obtained the same conclusion.⁵⁾ The present work shows nickel ions are also stabilized in octahedral coordination under the conditions for catalytic reaction.

Copper ion; The observed value of magnetic moments of copper ions shows they are in divalent state on silica gel surface evacuated at 300°C. Though the magnetic moments of copper ions are known to be slightly different with coordination,¹²⁾ they can not be a distinct criterion of structures.⁹⁾ On the other hand, g values determined from ESR spectra reflects coordinated state of copper ions precisely. Hecht derived equations for g values for $3d^1$ and $3d^9$ ions and shows that when copper ions are surrounded by square planar or distorted octahedral (elongated to z -axis) crystal field, g -values are expressed as follows.¹³⁾

$$g_{\parallel} = g_e(1 - 4\lambda/A_1) \quad g_{\perp} = g_e(1 - \lambda/A_2)$$

where $g_e = 2.0023$, λ : spin-orbit coupling constant, A_1 and A_2 are energy differences between ground state ($d_{x^2-y^2}$) and excited states (d_{xy} and d_{yz} , respectively). From the equations

$$\frac{g_{\parallel} - g_e}{g_{\perp} - g_e} = 4 \frac{A_2}{A_1}$$

is followed and the ratio is expected to be about 4, as A_2 should be somewhat larger than A_1 .

With substitution of g_{\parallel} and g_{\perp} by the observed values, the ratio became 4.34 which is very probable value. Therefore, it can be concluded that copper ions are stabilized in tetragonal field.

Zinc ion; In the present research, experimental results to discuss the coordination of zinc ions were not obtained, but judging from the results of another metal ions investigated here, zinc ions may be assumed to be stabilized in either distorted octahedral or tetrahedral field. Generally, it is known zinc ions favorably form tetrahedral complexes.¹⁴⁾ So zinc ions on the silica gels may be assumed to be stabilized in tetrahedral coordination and two of four ligands are surface siloxane ions. If the distance of adjacent siloxane ions are calculated assuming the surface of silica gel to be tetrahedral structure formed by silicone and oxygen (the distance of Si-O is 1.83 Å), the value 5.95 Å is obtained. The value suggests zinc ions exist in fairly distorted tetrahedrally coordinated state.

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